EFFECT OF FERRIC OXIDE CATALYST ON THE CRACKING OF POLYSTYRENE AND POLYETHYLENE

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INTRODUCTION

Investigations on waste plastic recycling are receiving public attentions mainly because of the increasing pressure of disposal problems from the ascending consumption of plastics. Our previous study [1] demonstrated that, at 440 °C and 60 min reaction time, liquid-phase cracking using tetralin and n-decane solvents increased oil yields from polystyrene (PS) but decreased oil yields from high-density polyethylene (HDPE), when compared to the crackings in solvent-free environment. Significant oil yield synergism was further observed for the cracking of PS and HDPE mixtures when sufficient hydrogen stabilization from the solvent was absent.

Our research continued to study the type of catalyst that may be applied to the liquid-phase cracking of plastics. This communication reports the effects of an Fe_2O_3/S catalyst, which is known for hydrogenolysis activities, on the liquid-phase cracking of PS and HDPE and their 50/50 mixtures.

EXPERIMENTAL

Figure 1 illustrates the experimental scheme of the liquid-phase cracking using a batch-mode 300-mL autoclave reactor. The plastics used were commercial-grade pellets of PS and HDPE. Reagent-grade tetralin, n-decane (n-C10) and decalin (cis- and trans- mixture) were used as the solvent for liquid-phase cracking without further purification. For catalytic runs, powders of 3 wt% iron(III) oxide and 2.4 wt% sulfur, both based on the total weight of feed plastics, were added.

A total weight of 80 g of feed reactants including the plastics and the liquid solvent, if used, was charged for each autoclave reaction experiment. The concentration of the plastics in each experiment with solvent feed was generally 25 wt% except for the cases investigating the effect of decalin dilution on PS and HDPE crackings. Experiments were also performed under solvent-free environment for comparison purposes. For mixtures of PS and HDPE, the ratio of PS to HDPE was 1/1 on a w/w basis. After being charged with feed reactants, the reactor was purged and then filled with nitrogen gas for non-catalytic runs, or with hydrogen gas for catalytic runs. The initial pressure was 4.0 MPa (570 psig) at ambient temperatures. The reaction was conducted at 440 °C for 60 min with constant stirring at 1000 rpm.

The volume of produced gases was measured using a wet gas meter and the composition analyzed using a GC equipped with a TCD. The yield and the average molecular weight of gaseous products were determined based on the gas volume measured and the gas composition analyzed. The product liquid slurry was distilled under a vacuum pressure as low as 1 torr at 330 °C. The recovered liquid distillate was further analyzed using another GC equipped with a 50-m long glass capillary column (Hewlett Packard Ultra-1) and an FID. The oven temperature of the GC unit was controlled starting from 60 °C at a 3.0 °C/min rate to 300 °C, at which it was kept isothermally for a period of 30 min. A GC-MS was used to assist the identification of the components of interest.

The total conversion was determined according to the following equation:

$$\text{total conversion, wt\%} = 100\% - \frac{\text{wt. of vacuum residue - wt. of catalyst as FeS}}{\text{net wt. of feed plastics}}$$

The oil yield was calculated by subtracting gas yield from the total conversion. For catalytic runs, the catalyst was assumed to have transformed to FeS after the reactions. The hydrogen consumption was calculated by determining the loss of hydrogen in the charged hydrogen gas less the amount consumed for the formation of hydrogen sulfide.

RESULTS AND DISSCUSSION

Cracking of PS

As illustrated in Table 1, the total conversion at 440 °C of the non-catalytic thermal runs was found to follow the order that tetralin > decalin > n-decane > solvent-free. The hydrogen donation capabilities of decalin and n-decane are essentially negligible, as compared to that of tetralin. Figure 2 shows the effect of decalin dilution, in terms of PS feed concentration, on the conversion and product selectivity. At a high temperature of 440 °C, secondary reactions quickly transform styrene, which is considered the primary product of PS cracking [2, 3], to products such as ethylbenzene, toluene, and cumene. With the increased interactions among reactive species, condensation reactions could prevail during the PS cracking. For the solvent-free case, the interactions among product species were the most intensive and the conversion could not be improved in the absence of sufficient hydrogenation. Results from GC-MS analysis of the oil fractions show that components such as terphenyls, quarterphenyls, and polyphenyls of higher order might have formed in the heavy fractions.

At 440 °C, tetralin not only buffered but also quickly stabilized reactive species by hydrogenation. For the case of catalytic cracking using Fe_2O_3/S catalyst and decalin solvent, the total conversion increased to completion with a low gas yield of 0.6 wt%. The high conversions obtained for the cracking in tetralin and catalytic hydrogenation environments suggest that hydrogen stabilization could promote PS conversion to produce light oil.

The gas yields from PS cracking were generally low except when using n-decane as the solvent. Substantial amounts of C1-C4 n-alkanes were produced in gaseous products when n-decane was used as the solvent at 440 °C. This suggests that n-decane could be susceptible to decomposition during PS cracking.

Cracking of HDPE

Typical product yields of HDPE cracking in the different reaction environments are presented in Table 2. At 440 °C, HDPE cracking shows the trend opposite to PS cracking by giving decreased total conversions in the presence of the solvents. This is mainly due to the different cracking mechanisms of HDPE and PS. At 440 °C, HDPE decomposition slowly produces a series of successive n-alkanes and α-alkenes. For the solvent-free environment, intensive interactions led to a moderately high conversion of 55.6 wt%. However, for the cracking in tetralin solvent environment, the total conversion was sharply reduced to a negligible level. At 440 °C, tetralin appeared to stabilize decomposition radical fragments at quite fast rates, slowing down the production of distillate oil from HDPE. The use of n-decane and decalin non-donor solvents under nitrogen atmosphere also significantly suppressed HDPE decomposition by dispersing the interactions among reactive species. The order of average molecular weight (MW) of gaseous products follows the same trend for the cracking in both PS and HDPE under the non-catalytic environments, showing that n-decane > solvent-free > decalin > tetralin. It is evident that tetralin effectively reduced the chances of further interactions. When n-decane was used as the solvent for HDPE cracking, small amounts of n-alkanes and α-alkenes with the carbon chain lengths less than 7 were produced, suggesting that n-decane could also be susceptible to decomposition during the HDPE cracking.

The cracking of HDPE using Fe_2O_3/S catalyst under hydrogen atmosphere in decalin solvent gave a total conversion substantially higher than that of the corresponding non-catalytic run. This indicates that the catalyst may have a cracking activity to increase the rate of HDPE decomposition to produce distillate oil in heavy fraction. The hydrogen consumption was low, and the catalyst showed quite different behaviors from tetralin in that the catalyst was able to hydrogenate α-olefins and showed cracking activity with HDPE. Only small concentrations of α-olefins and branched alkanes were found in the oil fraction obtained from the catalytic run.

The effect of decalin dilution on product selectivity of HDPE cracking is illustrated in Figure 3. As the HDPE feed concentration increased, both the oil and gas yields also increased. However, a decrease in total conversion did not occur for high HDPE feed loadings. Although black soot-like material was observed on the reactor wall and around stirrer shaft surfaces, occurrence of condensation reactions in HDPE cracking at 440 °C appeared not as severe as in PS cracking. Unlike PS, HDPE does not readily convert to its monomer precursor. When a normal alkane molecule is decomposed, it

probably first converts to a pair of n-alkane and α-alkene, which may or may not have the same chain lengths. Figure 3 indicates that, as the conversion becomes greater, the selectivity increases for lighter n-alkanes whereas it remains relatively constant or slightly decreases for lighter α-alkenes under the non-catalytic environment. The carbon distribution pattern further indicates that HDPE cracking may start with random cleavage on the carbon-carbon main chains and then followed by β-scission to the free radical positions, producing n-alkanes and α-alkenes of various chain lengths.

Cracking of PS and PE Mixtures

Table 3 presents the results of non-catalytic and catalytic liquefaction runs for 50/50 PS and PE mixtures at 440 °C for 60 min. For the non-catalytic thermal runs, strong interactions among the cracking products from PS and HDPE mixtures result in oil yield synergism [1]. The results further show that the combination of Fe_2O_3 and sulfur provides an effective way for hydrogenation, simply by judging from the hydrogen consumed from the gas phase. The order of hydrogen consumption based on the charged H_2 agrees well with the hydrogen need during the plastics cracking. The solvent-free run required the most hydrogen because of its high concentration (i.e., 100 wt%) of the mixed plastics, when compared with other runs that used 25 wt% loading with a solvent medium. The catalytic run using tetralin as the solvent consumed the least amount of hydrogen from the gas phase, due to the affluent hydrogen supply from the solvent. For those runs using decalin and n-decane as the solvent media, their hydrogen consumption requirements were intermediate.

In Table 3 except the case using n-decane solvent, the total conversions and C5-C9 n-alkanes yields decreased by the application of Fe_2O_3/S catalyst. This is attributed to the effective catalytic hydrogenation that is able to stabilize reactive species and suppress the oil yield synergism. The catalyst clearly exhibited its activities increasing the selectivity for light aromatic components produced from the PS cracking, stabilizing the reactive species, and suppressing HDPE from induced cracking.

When n-decane was used as the solvent, the production of C5-C9 n-alkanes was exceedingly high from both the non-catalytic and catalytic runs, when compared to other reaction environments. The total conversion of the catalytic run was not decreased but slightly increased. This may be explained as a combined result of induced and accelerated cracking of HDPE by PS decomposition products, n-decane cracking, and the cracking and hydrogenation activities of the catalyst.

PS decomposes to styrene at a temperature as low as 400 °C. As indicated in Table 1, the cracking of PS could significantly induce the cracking of n-decane below a temperature at which the hydrogenation could take place to stabilize reactive species. Other solvents such as tetralin and decalin are more stable than n-decane and were not susceptible to PS-induced cracking into reactive species. Moreover, it is also noted that the slow cracking of HDPE at 440 °C might also slightly induce the cracking of n-decane, or vice versa, under the non-catalytic condition. Under the combined effect, the decomposition of HDPE could be induced and accelerated by the presence of reactive species from both n-decane and PS cracking, giving the high yields of C5-C9 n-alkanes and n-alkylbenzenes with C6-C9 side chains.

When using the Fe_2O_3/S catalyst, although slightly more cracking could occur for HDPE to produce oils in heavy fraction, there also exists a hydrogen stabilization effect from the gas phase counteracting the induced cracking of HDPE. This leads to an overall result of slightly increases in total conversion and oil yield. The GC chromatogram indicates that less concentrations of α-olefins and branched alkanes were contained in the oil produced from the catalytic runs. Interaction products such as n-alkylbenzenes with C6-C9 side chains were also present in the oil fractions but generally in smaller yields.

PS cracking at 440 °C could proceed much faster than the effective hydrogenation. For the major products from PS, ethylbenzene selectivity was sharply increased and became the most dominant component probably due to direct hydrogenation to the styrene during both liquid- and gas-phase hydrogenations. The trend for other components also follows in similar fashions for their variations, namely, the selectivity for cumene increased while for toluene decreased.

The rate of HDPE cracking may be slowed down to an extent depending on the reaction environment either by using tetralin solvent or Fe_2O_3/S catalyst in hydrogen atmosphere. Tetralin was able to stabilize decomposition free radicals but was not as

effective as the catalyst in the hydrogenation of unsaturated bonds. There would need significantly additional hydrogen supply if HDPE could have been cracked effectively. The existence of oil yield synergism produces more varieties of components by increased interactions. The catalytic cracking of PS and HDPE mixtures in n-decane solvent showed a high conversion with a low gas yield.

CONCLUSIONS

Fe_2O_3/S catalyst showed a hydrogenation activity for the cracking of PS in a non-hydrogen donor solvent at 440 °C to yield a total conversion of 100 wt%. It demonstrated an effective way of converting PS using liquid-phase cracking and a hydrogenation catalyst. The catalyst slightly increased the conversion of HDPE under a similar condition by exhibiting cracking and hydrogenation activities. When used in the cracking of PS and HDPE mixtures, the catalyst decreased total conversions by suppressing interactions among reactive products under solvent-free, tetralin, and decalin environments. When n-decane was used as the solvent for the cracking of PS and HDPE mixtures, the catalyst was able to maintain effective decomposition of PS and HDPE, and give a decreased gas yield in hydrogen atmosphere.

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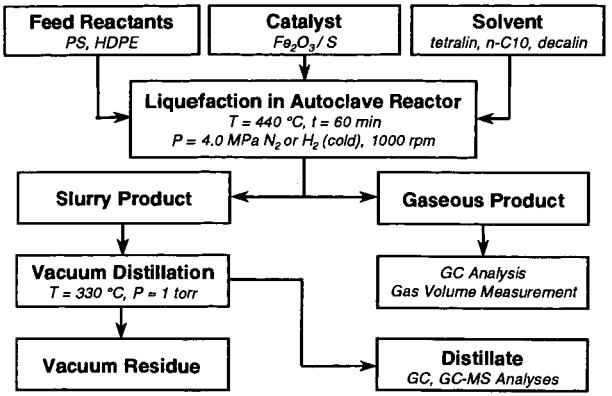

Figure 1. Schematic Illustration of Plastics Liquefaction Experiment

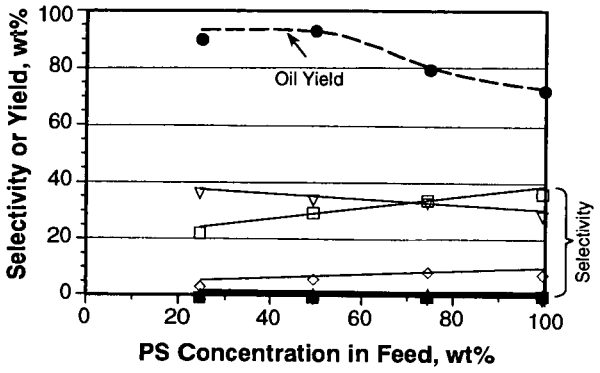

Figure 2. Effect of Decalin Solvent Dilution on PS Cracking at 440 °C and 60 min (Legend: □ ethylbenzene ◇ cumene ▽ toluene △ propylbenzene ■ benzene ▼ styrene ● oil)

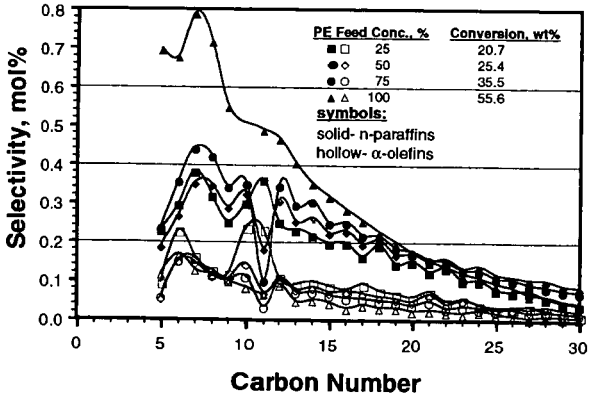

Figure 3. Effect of Decalin Dilution on PE Cracking at 440 °C and 60 min

Table 1. Product Yields of PS Cracking in Different Reaction Environments at 440 °C

Reaction Environment	Non-Catalytic, N_2				Catalytic, H_2
	Solvent-Free	Tetralin	Decalin	n-Decane	Decalin
Total Conversion, wt%	**73.2**	**96.5**	**91.8**	**89.0**	**100.0**
Oil Yield, wt%	**72.9**	**95.8**	**90.8**	**83.8**	**99.4**
benzene, wt%	0.9	0.2	0.4	0.7	0.7
toluene, wt%	21.6	40.8	33.8	33.3	24.4
ethylbenzene, wt%	27.4	27.7	21.2	13.4	41.4
styrene, wt%	0.0	0.5	0.4	0.5	0.0
cumene, wt%	6.6	5.5	4.1	3.7	8.3
propylbenzene, wt%	1.3	1.5	1.4	1.6	1.6
Gas Yield, wt%	**0.3**	**0.7**	**1.0**	**5.1**	**0.6**
Gas MW (average)	18.1	5.6	10.2	30.2	28.7
Hydrogen Consumption‡					
wt% of plastics					0.8
wt% of H_2 charged					18.4

Table 2. Product Yields of HDPE Cracking in Different Reaction Environments at 440 °C

Reaction Environment	Non-Catalytic, N_2				Catalytic, H_2
	Solvent-Free	Tetralin	Decalin	n-Decane	Decalin
Total Conversion, wt%	**55.6**	**1.1**	**20.7**	**24.8**	**38.5**
Oil Yield, wt%	**53.9**	**1.0**	**20.1**	**22.6**	**37.8**
C5-C9 n-alkanes, wt%	6.8	0.1	1.1	8.7	0.9
Gas Yield, wt%	**1.7**	**0.1**	**0.6**	**2.2**	**0.7**
Gas MW (average)	27.5	5.5	22.6	31.3	45.1
H_2 Consumption‡					
wt% of plastics					0.1
wt% of H_2 charged					1.8

Table 3. Results of Non-Catalytic Thermal and Catalytic Liquefaction Runs for 50/50 PS and PE Mixtures at 440 °C for 60 min

Reaction Environment	Solvent-Free		Tetralin		Decalin		n-Decane	
	Thermal	Catalytic	Thermal	Catalytic	Thermal	Catalytic	Thermal	Catalytic
Total Conversion, wt%	**81.5**	**70.2**	**55.6**	**51.6**	**78.4**	**66.6**	**76.0**	**79.4**
Oil, wt%	**80.3**	**69.1**	**55.1**	**51.2**	**76.8**	**65.9**	**72.7**	**77.2**
C5-C9 n-alkanes	5.9	1.4	0.4	0.2	2.1	1.0	17.6	17.8
n-alkylbenzenes with C6-C9 side chains	1.1	0.2	0.3	0.2	1.1	1.0	3.9	1.0
Toluene, wt%	19.9	14.2	19.4	5.7	19.1	13.2	20.4	12.5
Ethylbenzene, wt%	16.4	21.6	12.7	29.4	8.1	21.5	5.1	23.3
Cumene, wt%	3.3	4.8	2.7	5.2	1.1	4.2	0.8	2.0
Gas, wt%	**1.2**	**1.1**	**0.5**	**0.4**	**1.6**	**0.7**	**3.2**	**2.1**
Gas MW (average)	23.2	36.0	4.4	41.7	15.9	33.7	28.1	33.0
H_2 Consumption‡								
wt% of plastics		0.6		0.4		0.7		0.9
wt% of H_2 charged		**50.S**		**9.1**		**17.0**		**20.9**

Note: ‡ Not including contribution from feed solvent